

Removal of Arsenic(III) from Contaminated Waters using Iron(II) and Citrate¹

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Abstract. Contamination of water by arsenic both as a result of natural and anthropogenic processes poses a major threat to human health and to the environment in general. Where arsenic occurs as As(III), typical treatment involves peroxide oxidation to As(V), followed by coprecipitation and adsorption with iron(III). Because iron(II) commonly occurs concomitantly with arsenic in contaminated water, these waters have the potential to be self-treating when the Fe(II) oxidises and precipitates. However, As(III) oxidises much more slowly than Fe(II) at circumneutral pH, and As(III) does not coprecipitate to the same extent as As(V). A recently emerging technology for arsenic removal from drinking water in lesser developed countries involves the addition of citric acid to the Fe(II)/As(III) bearing water in the presence of sunlight. This has been found to promote the oxidation and coprecipitation of arsenic with iron. The aim of this paper is to examine this promising treatment technology further. The effect of pH on the removal of arsenic by iron(II) and citrate was examined. The photo-catalysed oxidation of As(III) in the presence of Fe(II) citrate and subsequent coprecipitation with the product Fe(III) is compared to the efficiency of arsenic removal by iron oxidation and precipitation alone. At pH 6-9, an arsenic:iron:citrate ratio of approx. 1:19:2 was found to reduce arsenic concentration from 1mg/L to <50µg/L after two hours of irradiation with light levels mimicking those found at the equator. The addition of citrate and illumination with UV light was found to increase the rate of iron(II) oxidation and the subsequent formation of precipitates.

Additional Key Words: Photocatalysis, coprecipitation, water treatment

¹Paper was presented at the 2009, Securing the Future and 8thICARD, June 22-26, 2009, Skellefteå, Sweden.

INTRODUCTION

Arsenic is 20th most abundant element on Earth. Contamination of groundwater is widespread affecting many areas of the world including Bangladesh, India, Vietnam, Thailand and Chile (Nordstrom, 2002). Arsenic often makes its way into water courses by the natural processes of weathering and dissolution of minerals such as arsenopyrite. Anthropogenic activities,

particularly mining and related industries can also introduce arsenic rich effluents into the environment if not carefully monitored and controlled.

The damaging effects of arsenic on health are wide ranging with arsenic poisoning being linked to neurological, dermatological and gastrointestinal problems (Hughes, 2002) as well as being a known carcinogen (U.S. Environmental Protection Agency, 1999). Limits set by the U.S. Environmental Protection Agency and the World Health Organisation (WHO) state that arsenic concentration should not exceed 10µg/l in drinking water, yet in many areas of the world populations are exposed to concentrations several orders of magnitude greater than this (Nordstrom, 2002).

Arsenic can exist in a range of oxidation states from -3 to +5 though it is most commonly found as As(III) or As(V) oxyacids in aqueous solution. It is known that As(III) is both more toxic (Ferguson and Gavis, 1972) and more mobile than As(V) (Amin et al., 2006). Oxidants such as H₂O₂ and Cl₂ are commonly used in pre-oxidation steps which maximise the concentration of As(V) relative to As(III) thus facilitating arsenic removal in subsequent processes (Amin et al., 2006).

Numerous methods have been developed for arsenic remediation, most commonly using adsorbents such as activated carbon (Borah et al., 2008) or aluminium oxide (Jeong et al., 2007) or co-precipitation with iron oxides (Cidarelli et al., 2008) to form sludges. Indeed in situations where iron and arsenic occur concomitantly (which is often the case) waters can be at least partially self treating (Hug et al., 2001) (Sarkar et al., 2008) as a result of in situ iron oxide precipitation.

One low tech and inexpensive method of arsenic remediation that takes advantage of naturally occurring dissolved iron is the SORAS (Solar Oxidation and Removal of ArSenic) method developed by Hug et al. (2001). This method requires the addition of citrate in the form of lemon juice to contaminated waters, followed by exposure to bright sunlight. Photolysis of the iron citrate complex enhances the rate of oxidation of As(III) to As(V) and hence increases the percentage uptake of arsenic by the subsequent formation of iron oxide precipitates.

Table 1. Summary of reactions involved in arsenic oxidation by dissolved Iron

Reaction	N ^o
$\text{Fe}^{\text{II}} + \text{O}_2 \rightarrow \text{Fe}^{\text{III}} + \text{O}_2^{\cdot-}$	1
$\text{Fe}^{\text{II}} + \text{O}_2^{\cdot-} + 2\text{H}^+ \rightarrow \text{Fe}^{\text{III}} + \text{H}_2\text{O}_2$	2
$\text{Fe}^{\text{II}} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{\text{III}} + \text{OH}^{\cdot} + \text{OH}^-$	3
$\text{Fe}^{\text{II}} + \text{OH}^{\cdot} \rightarrow \text{Fe}^{\text{III}} + \text{OH}^-$	4
$\text{Fe}^{\text{II}}\text{Cit} \leftrightarrow \text{Fe}^{\text{II}} + \text{Cit}$	5
$\text{Fe}^{\text{III}}\text{CitOH}^- + h\nu \rightarrow \text{Fe}^{\text{II}} + 3\text{-HGA}^{\cdot 2-} + \text{CO}_2 + \text{OH}^-$	6
$3\text{-HGA}^{\cdot 2-} \text{Fe}^{\text{III}}\text{OH}^{2+} \rightarrow 3\text{-OGA}^{2-} + \text{Fe}^{\text{II}} + \text{H}_2\text{O}$	7
$\text{As}^{\text{III}} + \text{O}_2^{\cdot-} + 2\text{H}^+ \rightarrow \text{As}^{\text{IV}} + \text{H}_2\text{O}_2$	8
$\text{As}^{\text{IV}} + \text{O}_2 \rightarrow \text{O}_2^{\cdot-} + \text{As}^{\text{V}}$	9

Reactions 1-4 from (King et al., 1995), reactions 5-9 from (Hug et al., 2001)

Many of the countries affected by arsenic waste from mining activities, including Malaysia, the Philippines, Thailand, Ecuador and Brazil (Williams, 2001) are situated on or near the Equator and experience relatively high levels of UV radiation throughout the year. Field trials were successfully carried out using the SORAS method in Bangladesh (Hug et al., 2001) showing that where natural sunlight is sufficiently intense no external source of energy other than for mixing is required.

Reactions 1-3 in Table 1 show how the conversion of Fe(II) to Fe(III) produces a number of different oxidising species (O_2^- , H_2O_2 , OH^*) capable of increasing the rate of As(III) oxidation. Reactions 5-7 show citrate photolysis occurring in several stages, with reactions 6 and 7 both regenerating Fe(II) (3-OGA and 3-HGA are the organic compounds oxy-glutarate and hydroxoglutarate respectively). The ability of citrate to form a soluble complex with Fe(III) facilitates the regeneration of Fe(II) and hence increases the rate of formation of highly oxidising species, catalysing arsenic oxidation via the two step process in reactions 8 and 9.

The aim of this study was to investigate the effect of pH on the ability of citrate to enhance arsenic removal by the mechanisms described above.

EXPERIMENTAL METHODS

Chemicals

All chemicals, As_2O_3 , $FeSO_4 \cdot 7H_2O$, $Fe_2(SO_4)_3$, C_6H_8O (citric acid) were laboratory grade from Fisher Scientific and were used as received. Stock solutions were prepared using high purity $18.0m\Omega$ water. All other solutions were prepared using Cardiff tap water.

Analysis

Arsenic and iron concentrations were measured on a PerkinElmer Optima 2100DV ICP-OES. All samples were filtered using Sartorius cellulose acetate membrane syringe end filters (26mm diameter, $0.45\mu m$ pore size) prior to analysis.

Preparation of As contaminated water.

Solid As_2O_3 was dissolved in 0.1M HCl to give a final concentration of 400mg/L. Aliquots of the stock solution were then added to Cardiff tap water and pH adjusted using 1M NaOH to obtain the desired pH and a final concentration of 1mg/L. Mixtures were stirred continuously. Once the desired pH was achieved solutions were stirred for one minute before addition of Fe(II) stock solutions.

Iron and citrate addition

Stock solutions containing 10g/L Fe(II) in 0.001M HCl and 10g/L Fe (II) in 0.02M citric acid were prepared. These were added to the As contaminated solutions to give initial Fe(II) concentrations in the range 2-12mg/L. The pH did not change by more than 0.1 units upon initial addition of the Fe(II) stock solutions. All reaction mixtures were stirred for 2 hours prior to sampling and analysis. At pH5, where iron precipitation did not go to completion in the time allowed samples were quenched with 1M HCl to prevent further precipitation prior to analysis.

Kinetic studies

Four samples were prepared containing 1.4mg/L As(III) at pH7. Fe(II) was added from acidic stock solution to two of the reaction mixtures to give an initial concentration of 6mg/L and total final volume of 1L. Fe(II) and citrate were added to the remaining two samples from a stock solution containing 10mg/L Fe(II) in 0.02M citric acid to give the same final volume

and Fe(II) concentration of 6mg/L. One sample with citrate and one without were exposed to UV light for two hours. The remaining two solutions were kept at the laboratory bench away from sources of UV light. All four mixtures were stirred continuously. 10ml samples were taken at regular intervals, passed through a syringe filter and immediately quenched with 10ml of 0.1M HCl.

UV illumination

In order to simulate solar radiation, experiments were carried out in the environmental chamber at Cardiff University, School of Engineering. The chamber was fitted with a Phillips MSR 6000 HR bulb and a custom made filter which resulted in a spectrum very similar to that of natural sunlight at the Earth's equator (Environmental Handbook for Defence Materiel). Illumination was started within 2 minutes of Fe(II) addition and all reaction mixtures were stirred continuously using magnetic stirrers.

Control experiments were carried out at the laboratory bench. Spectral readings were taken and it was determined that radiation in the region where dissolved Fe species strongly absorb (320-400nm) (Hug et al., 2001) was negligible. A comparison of the normalised spectra for the laboratory and the environmental chamber are shown below in Figure 1.

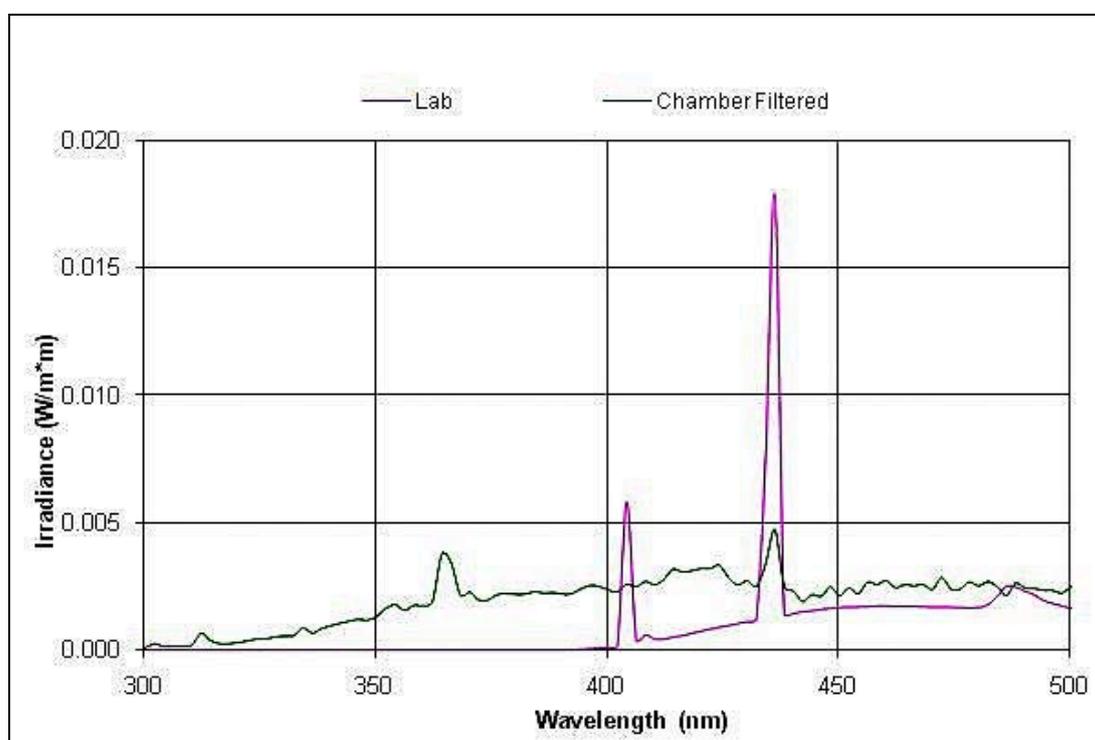


Figure 1. Normalised spectra taken at the laboratory bench and in the environmental chamber

RESULTS AND DISCUSSION

Kinetic studies

It can be seen from Figure 2, that at circumneutral pH irradiation with UV light significantly enhances arsenic removal with the addition of citrate yielding further improvements.

Several studies have shown that in natural systems sunlight promotes the reduction of Fe(III) to Fe(II) (Gammons et al., 2005) (Sullivan et al., 1998), which is observed as diel cycling of dissolved iron levels in acidic mountain streams. McKnight et al. (1998) have

suggested that in addition to generating highly oxidising species this cycling between the two oxidation states may promote an increase in the abundance of amorphous iron oxides relative to more crystalline precipitates. Any differences in the nature of the precipitates are likely to affect arsenic adsorption, which might in part account for the differences in arsenic removal efficiency.

Analysis of the reaction mixtures showed that in all cases dissolved iron concentrations had decreased to below 40µg/L by 45 min. After this time dissolved iron levels continued to decrease in the absence of UV light, whereas in both of the mixtures irradiated with UV light dissolved Fe levels remained at around 30µg/L. These slightly elevated levels of dissolved iron (most likely Fe(II)) can be explained by the photoreduction and dissolution of precipitated Fe(III), a phenomenon recorded by Waite and Morel (1984). This might account for the continued (slow) reduction in As levels after 45mins something also observed previously in similar studies (Hug et al., 2001) (Lara et al., 2006).

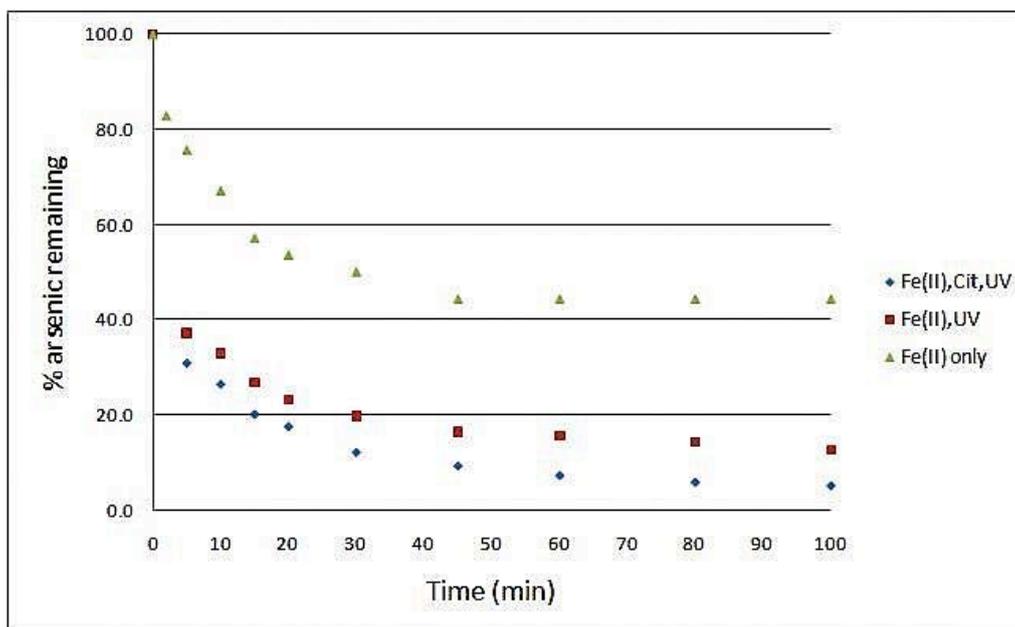


Figure 2. Reduction in arsenic concentration by Fe(II)

Effect of pH on As removal

The effect of pH on arsenic removal was much more significant where Fe(II) alone was added compared to the cases where citrate and UV light were also used. This can be seen from a comparison of the general trends shown in Figures 3 and 4 with the data being grouped closer together over the pH range studied in Figure 4. There is also greater scatter in the data in Figure 3 where small changes in pH of 0.1 or 0.2 points had a considerable influence on the results.

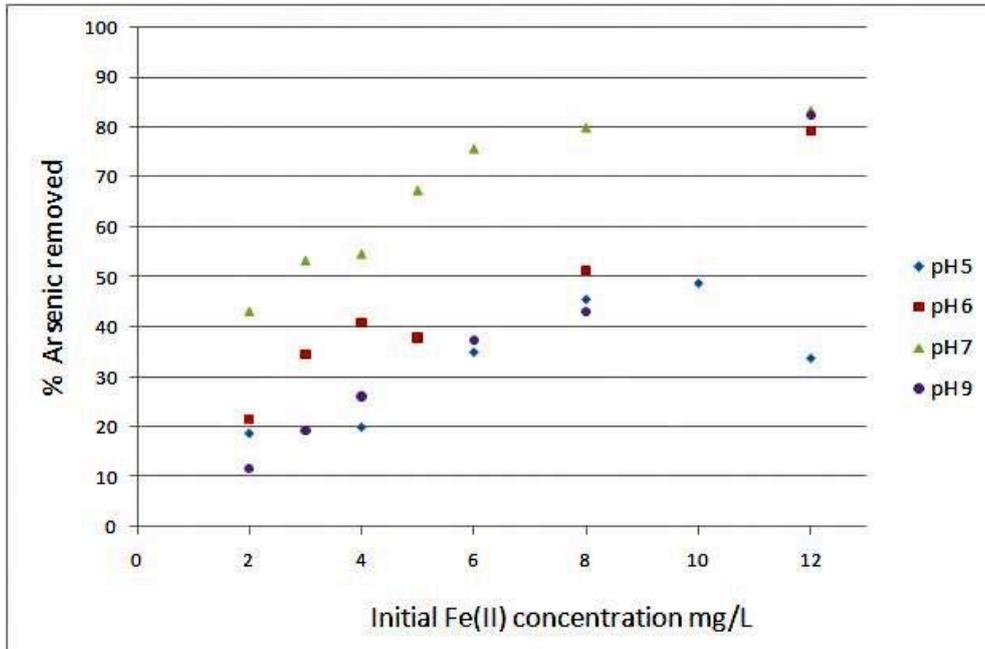


Figure 3. Percentage of As removed by Fe at pH 5-9

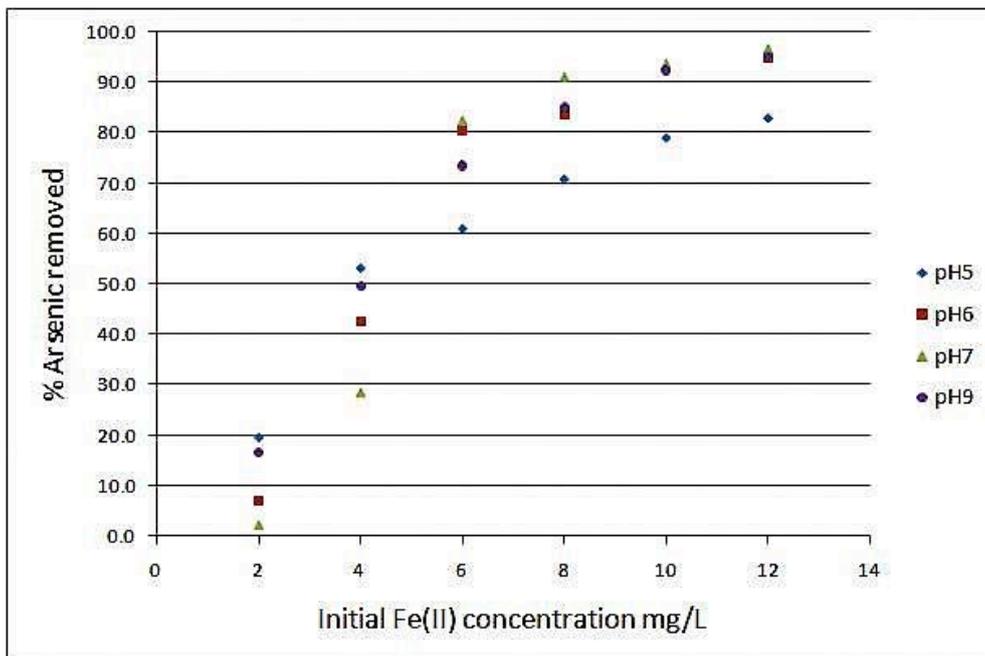


Figure 4. Percentage of As removed by Fe and citrate in the presence of UV light at pH 5-9

From Figure 3 the optimum pH for As removal appears to be around pH7, while there is no clear pattern relating arsenic removal to an optimal pH in Figure 4. The lack of correlation between pH and arsenic removal is most likely to be a result of several different pH dependent mechanisms. Changes in pH may alter the rate determining steps for arsenic oxidation and removal, as well as altering the amount of arsenic removed via co-precipitation compared to adsorption. It is known that arsenic oxidation occurs more rapidly at pH9 than at

pH7 and that the arsenic species present are more highly charged at this pH (Kartinen and Martin, 1995). Both of these factors tend to suggest that arsenic should be more readily removed from solution by both co-precipitation and adsorption at higher pH. However, at pH9 the high concentration of OH⁻ tends to make the surface of iron precipitates and dissolved iron complexes more negatively charged (Amin et al., 2006), so hindering the approach of the arsenate and arsenite anions. The relative importance of each of the many competing reactions over the pH range studied is not well documented. Hug et al. (2001) list 30 separate reactions and equilibria thought to occur between iron, citrate, arsenic oxyanions and numerous photo-generated radicals.

Overall, arsenic removal appeared to be least effective at pH5. Analysis of the reaction mixtures confirmed that this was due to a slower rate of iron oxide precipitation with 20-80% of iron remaining in solution after 2 hours. Figure 5 shows the actual mass of iron precipitated, illustrating that increases in initial Fe(II) concentration above 6mg/L resulted in only slight changes in the mass of precipitate produced after 2 hours. Surprisingly, arsenic removal did continue to increase measurably, particularly when citrate and UV light were used. Despite the fact that the mass of iron precipitated did not change by more than 0.5mg/L, when initial Fe(II) concentration increased from 4-12mg/L arsenic removal increased by around 30%. One possible explanation is that the increasing concentrations of dissolved Fe(II) and citrate increased the rate of As(III) oxidation and hence its rate of removal.

What is not known is whether the structure of the precipitate changed and how this may have influenced arsenic binding. It is also worth noting that in all cases where UV light was used, the presence of citrate resulted in more rapid precipitate formation than in the cases where no citrate was added.

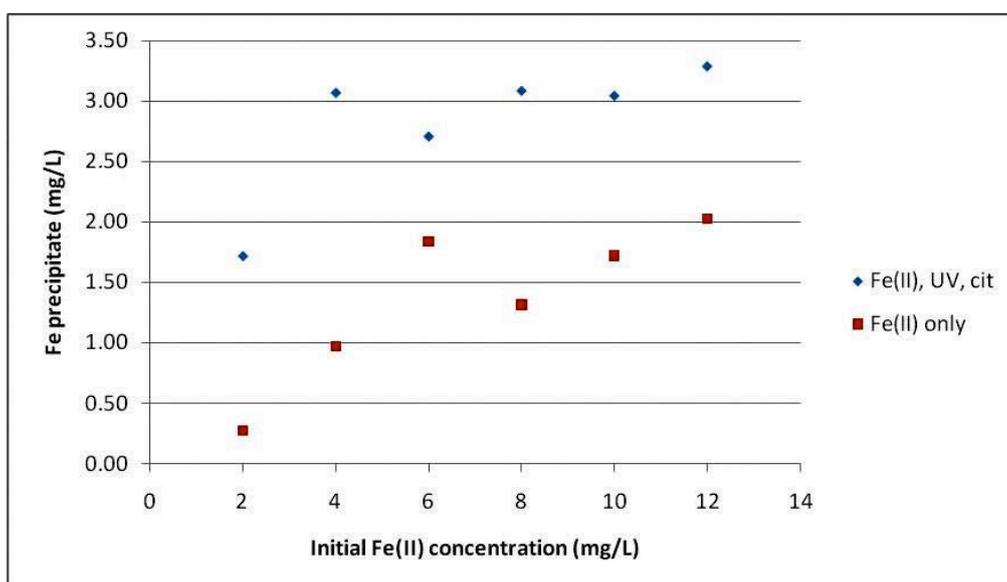


Figure 5. Mass of Fe precipitated after 2 hours vs initial Fe(II) concentration

The results obtained for arsenic removal using Fe(II) and citrate at circumneutral pH were in agreement with the work of other authors (Lara et al., 2006). The optimal ratio for arsenic removal found here for arsenic:iron:citrate was 1:18.6:2.1 compared to 1:18.7:4.5 for Lara et al. (2006). In addition to this (taking into account effects of pH, UV intensity and citrate concentration) there was also broad agreement between the kinetic studies.

CONCLUSIONS AND ENVIRONMENTAL SIGNIFICANCE

It has been shown that over the range 5-9, pH has little effect on the ability of iron to remove arsenic from solution in the presence of citrate and UV light. The major limiting factor is the rate of iron precipitation, with much of the iron remaining in solution after 2 hours at pH5. The surprising lack of pH dependence is likely to be a result of the complex nature of the chemistry involved. There are at least 30 individual reactions and equilibria occurring simultaneously (many of which are competing reactions) involving iron, citrate, arsenic and numerous radicals. While pH is likely to affect the rate of a number of these reactions the overall result in terms of arsenic removal remains the same. Further investigation of the species present is required in order to determine the dominant pathways occurring under acid, alkaline and circumneutral conditions.

The work here has confirmed the potential of the SORAS method as an effective and low tech way to remove arsenic from waters co-contaminated with iron. It has been shown that the technique is effective over a pH range which coincides with a significant proportion of the arsenic bearing mine water discharges around the World (Williams, 2001).

In addition to the already successful application of the SORAS technique to the treatment of drinking water this study has highlighted the potential of using iron(II) and citrate as part of an industrial scale water treatment process. Iron compounds are known to be effective sorbents for a number of heavy metals including cadmium, chromium, lead, mercury and copper, and can be used to simultaneously remove a number of contaminants from solution (Benhammou et al., 2004) (Genc-Fuhrman et al., 2008) (Ozverdi and Erdem, 2006). In the case of chromium it has been suggested that the presence of Fe(II) increases the rate of reduction of Cr(IV) to Cr(III), which subsequently precipitates with Fe(III) to form mixed hydroxides (Zhou et al., 2008). The effect of the photo-catalysed reaction between iron(II) and citrate on the removal of other heavy metals or combinations of heavy metals has not been studied, and may have applications in the remediation of acid mine waters of widely varying composition, storm waters and industrial waste waters.

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